

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC33

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This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.4 \pm 0.9) \times 10^{-12}$	298	Martínez et al., 1999	DF-LIF (a)
$(5.8 \pm 0.7) \times 10^{-12}$	433		
<i>Relative Rate Coefficients</i>			
$(1.31 \pm 0.04) \times 10^{-11}$	295	Atkinson et al., 1984	RR (b)
$(1.12 \pm 0.17) \times 10^{-11}$	298	Barnes et al., 1990	RR (c)

Limonene is 4-isopropenyl-1-methyl-cyclohexene.

### Comments

- $\text{NO}_3$  radicals ( $6\text{--}30 \times 10^{11} \text{ molecule cm}^{-3}$ ) generated from reaction of F atoms (made in a microwave discharge through  $\text{F}_2/\text{He}$ ) with  $\text{HNO}_3$ . Flow tube was operated at  $\sim 1.33 \text{ mbar}$  (1 Torr) He. Limonene was present at similar concentrations (1-3 fold) to  $\text{NO}_3$ . So that absolute  $\text{NO}_3$  concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.
- 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air.  $\text{NO}_3$  was generated by the thermal decomposition of  $\text{N}_2\text{O}_5$ . Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \text{limonene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 1.40 \pm 0.04$  is placed on an absolute basis by  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).
- 420 L glass chamber at 298 K and 980 mbar (735 Torr) of air.  $\text{NO}_3$  was generated by the thermal decomposition of  $\text{N}_2\text{O}_5$ . Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \text{limonene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 1.20 \pm 0.18$  is placed on an absolute basis by  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.2 \times 10^{-11}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.12$	298

### Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate studies, which indicate a larger rate coefficient than observed in the single absolute study.

The difference between the rate coefficients obtained at 298 and 433 K (factor 1.6) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

The reaction mechanism involves the initial addition of  $\text{NO}_3$  across a double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Product studies suggest that attack of  $\text{NO}_3$  at the exocyclic double bond of limonene is insignificant (Spittler et al 2006), which is supported by theoretical calculations (Jiang et al., 2009).

The final stable products in air include organic nitrates (largely unidentified but expected to include both mono- and dinitrates) with yields (per limonene reacted) between 30 and 67 % (Spittler et al. 2006; Hallquist et al., 1999; Fry et al 2011). The low yield of nitrate suggests that release of the nitrate functional group is significant, consistent with endolim being identified as the major reaction product (yield of 29 %, Spittler et al., 2006).

Secondary organic aerosol is formed at high yield in the smog-chamber studies of  $\text{NO}_3$  + limonene. Hallquist et al. (1999) quote a mass-based aerosol yield of 17 %, Fry et al (2011) ~ 30 %. Spittler et al. (2006) suggest that much of the organic aerosol is formed from further reactions of endolim.

### References

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